

Synthesis And Biological Activity Of New Acetylene Ethers Of Carbamates

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ABSTRACT

Research objective: to synthesize new carbamate derivatives - γ -bromopropargyl ethers of carbamate derivatives for their further application as initial compounds in the synthesis of simple and asymmetric diacetylene ethers of carbamate derivatives.

Materials and methods. Infrared spectra on UR-20 and UR-10 spectrometer ("Carl Zeiss", Germany) were applied at 3600-500 cm^{-1} , in the form of tablets pressed with KBr. For determination of purity of the obtained compounds, a thin layer chromatography was used. As an adsorbent we used a layer of Al_2O_3 of the II activity degree, and an iodine vapor as a developer.

Results and Discussion. Using the method of bromination of propargyl ethers of carbamate derivatives, γ -bromopropargyl ethers of carbamate derivatives were obtained, used in the synthesis of simple and asymmetric diacetylene ethers of carbamate derivatives. The optimal conditions for their synthesis were established in the process of studying the effect of various factors. Besides, antifungal and herbicide activity of the synthesized compounds was studied and analyzed. Compounds with high antifungal and herbicidal activity were determined.

Conclusion. Convenient methods were developed for obtaining new γ -bromopropargyl ethers of carbamate derivatives during the investigation. New simple diacetylene ethers of carbamate derivatives were synthesized by the reaction of interaction on the basis of propargyl ethers and γ -bromopropargyl ethers of carbamate derivatives. New asymmetric diacetylene ethers of carbamate derivatives were synthesized by carrying out the reaction of interaction based on propargyl ethers and γ -bromopropargyl ethers of various carbamate derivatives.

Key words: carbamates, propargyl ethers, γ -bromopropargyl ethers, simple and asymmetric diacetylene ethers, antifungal activity, herbicide activity.

1. INTRODUCTION

One of the main tasks of modern science is a targeted search for new highly effective and safe medicines [1,2]. In this regard, acetylene-containing compounds are of particular interest, since it is possible to obtain a wide variety of heterocyclic carbamate derivatives on their basis. Particularly, it is known that many heterocyclic carbamate derivatives have a wide spectrum of biological action [3,4,5,6]. They have potential to lower the blood pressure, can

lead to increased anticonvulsant properties, have psychotropic, muscle relaxant effects, as well as have different bactericidal activity, analgesic, antitussive and local anesthetic effects [7]. The presence of the acetylene bond and the carbamate function allows them to be used in various other fields of the national economy [8,9,10,11,12]. They can be used as valuable intermediate product for the synthesis of herbicides, fungicides, etc. [13,14]. So, for example, currently monuron, diuron, simazine, atrazine, meturin are used as herbicides [15,16]. Among these compounds, carbamate derivatives are active insecticides and herbicides [17, 18]. Butynyl carbamate is recommended as an herbicide, propargoxyphenyl-N-methyl carbamates are proposed as pesticides [19, 20]. In addition, highly effective physiologically active substances were identified among them: antiseptics, antispasmodics, antitumor, antiparasitic and antimicrobial medications [21, 22].

Thus, acetylene-containing carbamate derivatives are of particular interest for using as valuable intermediates for the synthesis of biologically active substances, creation of medicines, dyes and, what is very important, new generation of insectoacaricides.

At the same time, the known methods for their production are considered to be complex, multi-staged, based on the use of hard-to-reach, aggressive initial reagents, and accompanied by emitting of a large amount of hazardous waste. The yields of desired products are low, which makes it difficult to expand the boundaries of their industrial application.

Development of preparative methods for the synthesis of acetylene-containing carbamate derivatives from available reagents, the study of their properties for practical use in various fields of chemical science and practice is undoubtedly an urgent task.

Research Objective

The present work continues the study in the field of synthesis of new carbamate derivatives – synthesis of γ -bromopropargyl ethers of carbamate derivatives, for their further use as initial compounds in the synthesis of simple and asymmetric diacetylene ethers of carbamate derivatives.

2. MATERIALS AND METHODS

During the research infrared spectra on UR-20 and UR-10 spectrometer (“Carl Zeiss”, Germany) were applied at $3600-500\text{ cm}^{-1}$, in the form of tablets pressed with KBr.

A thin layer chromatography was used for determination of purity of the obtained compounds. As an adsorbent we used a layer of Al_2O_3 of the II activity degree, and as a developer - an iodine vapor.

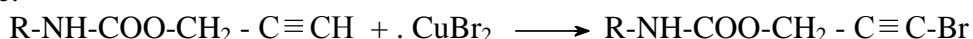
3. RESULTS AND DISCUSSION

To study the reactivity of terminal hydrogen in propargyl ethers of carbamate derivatives, we carried out a bromination reaction.

Substituting of acetylene hydrogen in propargyl ethers of carbamates by bromine is carried out with the participation of equimolar amounts of propargyl carbamates and CuBr_2 in an organic solvent.

We used γ -bromopropargyl ethers of carbamate derivatives in the synthesis of simple and asymmetric diacetylene ethers of carbamate derivatives.

In contrast to the hypohalous method, the bromination method is more accessible, since the reaction proceeds in one stage at room temperature in methanol according to the scheme:

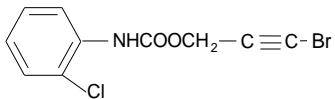
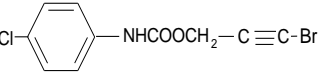
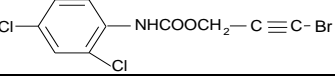
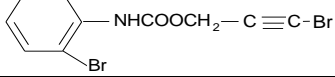
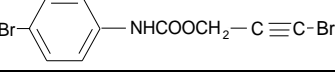
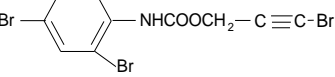
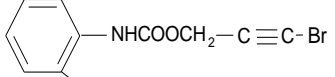
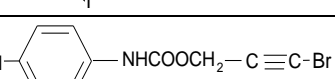


where: R= 2-Cl-C₆H₄(I); 4- Cl-C₆H₄(II); 2,4- Cl-C₆H₃(III); 2-Br-C₆H₄(IV); 4- Br-C₆H₄(V); 2,4-Br-C₆H₃(VI); 2-I-C₆H₄(VII); 4-I-C₆H₄(VIII);

The physiochemical characteristics of the synthesized compounds are presented in the Table 1.

Table 1.

Physiochemical characteristics of γ -bromopropargyl ethers of carbamate derivatives

| № | Formula | Yield % | Melting point, °C | Determined N, % | Chemical formula | Calculated N, % |
|---|---|---------|-------------------|-----------------|---|-----------------|
| 1 |  | 78 | 91-92 | 27,71 27,74 | C ₁₀ H ₇ NO ₂ ClBr | 27,73 |
| 2 |  | 79 | 81-82 | 21,71 27,73 | C ₁₀ H ₇ NO ₂ ClBr | 27,73 |
| 3 |  | 80 | 47-48 | 24,75 24,78 | C ₁₀ H ₆ NO ₂ Cl ₂ Br | 24,77 |
| 4 |  | 81 | 72-74 | 48,03 48,06 | C ₁₀ H ₇ NO ₂ Br ₂ | 48,05 |
| 5 |  | 83 | 63-65 | 48,04 48,05 | C ₁₀ H ₇ NO ₂ Br ₂ | 48,05 |
| 6 |  | 80 | 75-76 | 58,23 58,26 | C ₁₀ H ₆ NO ₂ Br ₃ | 58,25 |
| 7 |  | 84 | 80-81 | 21,03 21,06 | C ₁₀ H ₇ NO ₂ IBr | 21,05 |
| 8 |  | 83 | 81-82 | 21,04 21,05 | C ₁₀ H ₇ NO ₂ IBr | 21,05 |

The structure of the obtained compounds was proved by the data of elemental analysis and infrared spectroscopy.

The absorption band corresponding to valence vibrations of NH-group was observed in the infrared spectra of compounds at 3340cm⁻¹; the absorption band at 2230cm⁻¹ corresponded to the vibrations of the - C≡C-Br bond.

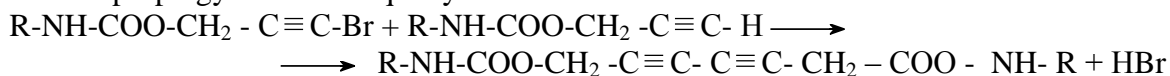
In contrast to the spectra of the initial propargyl ethers of carbamate, there was no absorption band corresponding to valence vibrations - C=CH in the obtained γ -bromopropargyl ethers in the spectra, which indicated the bromination reaction precisely due to active hydrogen.

The obtained γ -bromopropargyl ethers were used by us as initial compounds in the synthesis of simple and asymmetric diacetylene ethers of carbamate derivatives.

There are a great number of works devoted to the synthesis and study of acetylene derivatives of various organic substances. In the process of obtaining those compounds, various methods were applied: the Glaser method, the Zalkind and Fundiler method, the Eglinton method, the Chodkiewicz-Kadio method. Using those methods, the authors obtained diacetylene-containing derivatives of various compounds: hydrocarbons, ethers, nitrogen-containing diacetylenes, and others [21-22].

For obtaining of diacetylene ethers of carbamate derivatives we used the Chodkiewicz-Kadio method. The choice of this method is explained by the fact that it creates a possibility to obtain diacetylene ethers with a given structure and in a high yield.

Simple diacetylene ethers were obtained by the interaction of propargyl ethers and γ -bromopropargyl ethers of equally substituted carbamate derivatives:



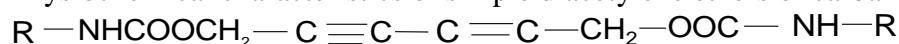
where: R= 2-Cl-C₆H₄(IX); 4-Cl-C₆H₄(X); 2,4-Cl-C₆H₃(XI); 2-Br-C₆H₄(XII); 4-Br-C₆H₄(XIII); 2,4-Br-C₆H₃(XIV); 2-I-C₆H₄(XV); 4-I-C₆H₄(XVI);

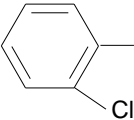
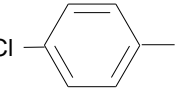
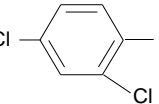
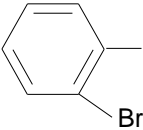
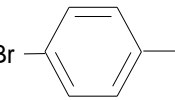
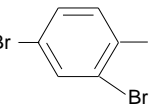
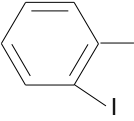
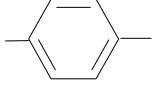
The structure of the synthesized compounds was proved by the data of elemental analysis and taking off of infrared spectra.

Physiochemical characteristics of simple diacetylene ethers of carbamate derivatives are presented in Table 2.

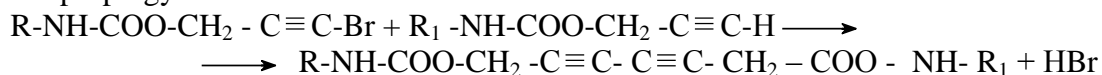
Table 2

Physiochemical characteristics of simple diacetylene ethers of carbamate derivatives



| No | R | Yield, % | Melting point, °C | Determined N, % | Chemical formula | Calculated N, % |
|----|---|----------|-------------------|-----------------|---|-----------------|
| 9 |  | 71,5 | 90-91 | 6,70 6,72 | C ₂₀ H ₁₄ N ₂ O ₄ Cl ₂ | 6,71 |
| 10 |  | 74,5 | 105-106 | 6,70 6,71 | C ₂₀ H ₁₄ N ₂ O ₄ Cl ₂ | 6,71 |
| 11 |  | 77,1 | 120-121 | 5,75 5,77 | C ₂₀ H ₁₂ N ₂ O ₄ Cl ₄ | 5,76 |
| 12 |  | 80,9 | 119-120 | 5,51 5,54 | C ₂₀ H ₁₄ N ₂ O ₄ Br ₂ | 5,53 |
| 13 |  | 83,5 | 125-126 | 5,52 5,55 | C ₂₀ H ₁₄ N ₂ O ₄ Br ₂ | 5,53 |
| 14 |  | 90,1 | 117-118 | 4,21 4,23 | C ₂₀ H ₁₂ N ₂ O ₄ Br ₄ | 4,22 |
| 15 |  | 84,7 | 122-123 | 4,66 4,68 | C ₂₀ H ₁₄ N ₂ O ₄ I ₂ | 4,67 |
| 16 |  | 85,2 | 115-116 | 4,66 4,69 | C ₂₀ H ₁₄ N ₂ O ₄ I ₂ | 4,67 |

Asymmetric diacetylene ethers were obtained by interaction of propargyl ethers and γ -bromopropargyl ethers of various carbamate derivatives:



where: R=2-Cl-C₆H₄ and R₁ = 4- Cl-C₆H₄(XVII);

R=2-Cl-C₆H₄ and R₁=2,4- Cl-C₆H₃(XVIII);

R=2-Cl-C₆H₄ and R₁=2-Br-C₆H₄(XIX);

R=2-Cl-C₆H₄ and R₁=4-Br-C₆H₄(XX);

R=2-Cl-C₆H₄ and R₁=2,4-Br-C₆H₃(XXI);

R=2-Cl-C₆H₄ and R₁=2-I-C₆H₄(XXII);

R=2-Cl-C₆H₄ and R₁=4-I-C₆H₄(XXIII);

R=4-Cl-C₆H₄ and R₁=2,4- Cl-C₆H₃(XXIV);

R= 4-Cl-C₆H₄ and R₁=2-Br-C₆H₄(XXV);

R= 4-Cl-C₆H₄ and R₁=2,4-Br-C₆H₃(XXVI);

R=4-Cl-C₆H₄ and R₁=2-I-C₆H₄(XXVII);

R=4-Cl-C₆H₄ and R₁=4-I-C₆H₄(XXVIII);

R=2,4- Cl-C₆H₃ and R₁=2-Br-C₆H₄(XIX);

R=2,4- Cl-C₆H₃ and R₁=4 -Br-C₆H₄(XXX);

R =2,4- Cl-C₆H₃ and R₁=2,4-Br-C₆H₃(XXXI);

R=2,4- Cl-C₆H₃ and R₁=2-I-C₆H₄(XXXII);

R =2,4- Cl-C₆H₃ and R₁=4 -I-C₆H₄(XXXIII);

R =2-Br-C₆H₄ and R₁=4- Br-C₆H₄(XXXIV);

R=2-Br-C₆H₄ and R₁=2,4-Br-C₆H₃(XXXV);

R=2-I-C₆H₄ and R₁=4-Cl-C₆H₄(XXXVI);

R=2-I-C₆H₄ and R₁ =2-Br-C₆H₄(XXVII);

R=2-I-C₆H₄ and R₁=4-Br-C₆H₄(XXVIII);

R=2-I-C₆H₄ and R₁=2,4-Br-C₆H₃(XXXIX);

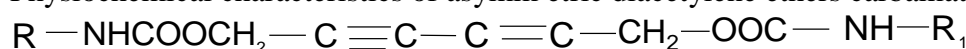
R=4-I-C₆H₄ and R₁ = 4-Br-C₆H₄(XXXX);

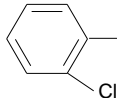
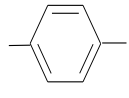
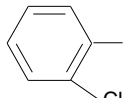
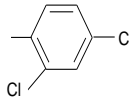
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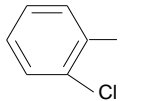
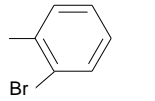
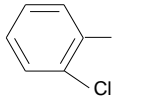
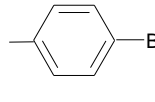
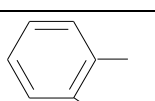
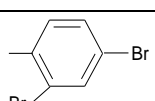
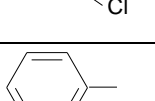
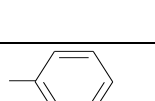
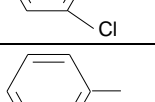
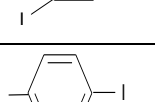
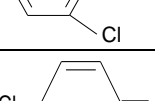
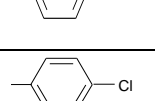
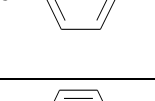
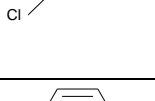
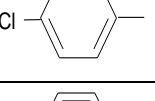
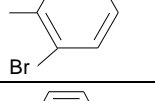
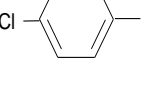
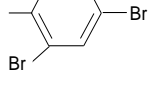
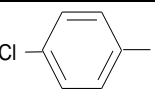
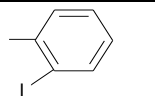
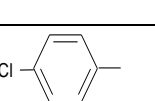
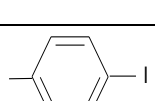
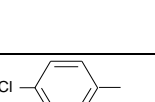
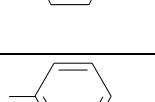
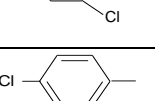
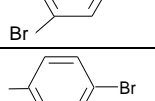
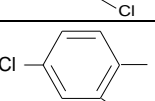
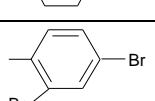
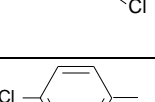
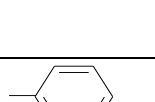
The physicochemical characteristics of asymmetric diacetylene ethers of carbamate derivatives are presented in the Table 3.

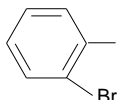
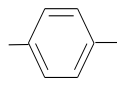
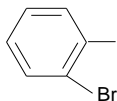
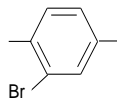
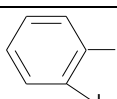
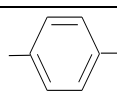
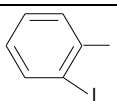
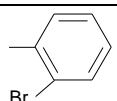
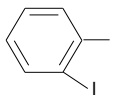
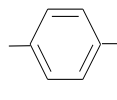
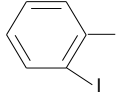
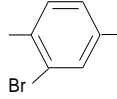
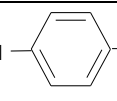
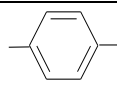
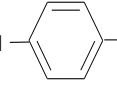
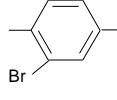
Table 3

Physicochemical characteristics of asymmetric diacetylene ethers carbamate derivatives



| No | R | R ₁ | Yield, % | Melting point, °C | Determined N, % | Chemical formula | Calculated N, % |
|----|---|---|----------|-------------------|-----------------|---|-----------------|
| 17 |  |  | 76.6 | 118-119 | 6,33 6,36 | C ₂₀ H ₁₄ N ₂ O ₄ Cl ₂ | 6.71 |
| 18 |  |  | 80.5 | 88-89 | 5,89 5,90 | C ₂₀ H ₁₃ N ₂ O ₄ Cl ₃ | 6.20 |

| | | | | | | | |
|----|---|---|------|---------|--------------|------------------------------|------|
| 19 |  |  | 78.2 | 95-96 | 5,76 5,78 | $C_{20}H_{14}N_2O_4ClBr$ | 6.07 |
| 20 |  |  | 81.3 | 104-105 | 5,76 5,79 | $C_{20}H_{14}N_2O_4ClBr$ | 6.07 |
| 21 |  |  | 78.5 | 120-121 | 4,94 4,97 | $C_{20}H_{13}N_2O_4ClBr_2$ | 5.18 |
| 22 |  |  | 79.8 | 119-120 | 5,25 5,27 | $C_{20}H_{14}N_2O_4ClI$ | 5.51 |
| 23 |  |  | 80.5 | 122-123 | 5,25 5,28 | $C_{20}H_{14}N_2O_4ClI$ | 5.51 |
| 24 |  |  | 73.4 | 85-86 | 6,18 6,21 | $C_{20}H_{13}N_2O_4Cl_3$ | 6.20 |
| 25 |  |  | 78.1 | 97-98 | 6,04 6,08 | $C_{20}H_{14}N_2O_4ClBr$ | 6.07 |
| 26 |  |  | 71.9 | 88-89 | 5,16 5,19 | $C_{20}H_{13}N_2O_4ClBr_2$ | 5.18 |
| 27 |  |  | 70.3 | 91-93 | 5,51 5,53 | $C_{20}H_{13}N_2O_4ClI$ | 5.52 |
| 28 |  |  | 72.2 | 105-106 | 5,51 5,54 | $C_{20}H_{13}N_2O_4ClI$ | 5.52 |
| 29 |  |  | 80.3 | 100-101 | 5,64 5,66 | $C_{20}H_{13}N_2O_4Cl_2Br$ | 5.65 |
| 30 |  |  | 74.1 | 111-112 | 5,65 5,66 | $C_{20}H_{13}N_2O_4Cl_2Br$ | 5.65 |
| 31 |  |  | 72.7 | 120-121 | 4,86 4,88 | $C_{20}H_{12}N_2O_4Cl_2Br_2$ | 4.87 |
| 32 |  |  | 75.6 | 115-116 | 5,14 5,17 | $C_{20}H_{13}N_2O_4Cl_2I$ | 5.16 |
| 33 |  |  | 77.7 | 119-112 | 5,14 5,16 | $C_{20}H_{13}N_2O_4Cl_2I$ | 5.16 |

| | | | | | | | |
|----|---|---|------|---------|--------------|---------------------------|------|
| 34 |  |  | 70.2 | 81-83 | 5.50 5.54 | $C_{20}H_{14}N_2O_4Br_2$ | 5.53 |
| 35 |  |  | 70.7 | 87-88 | 4.85 4.88 | $C_{20}H_{13}N_2O_4Br_3$ | 4.87 |
| 36 |  |  | 75.6 | 99-100 | 5.50 5.52 | $C_{20}H_{14}N_2O_4ICl$ | 5.51 |
| 37 |  |  | 78.2 | 105-106 | 5.04 5.07 | $C_{20}H_{14}N_2O_4IBr$ | 5.06 |
| 38 |  |  | 72.1 | 103-104 | 5.06 5.08 | $C_{20}H_{14}N_2O_4IBr$ | 5.06 |
| 39 |  |  | 80.3 | 110-111 | 4.41 4.44 | $C_{20}H_{14}N_2O_4IBr_2$ | 4.43 |
| 40 |  |  | 79.7 | 118-119 | 5.06 5.08 | $C_{20}H_{14}N_2O_4IBr$ | 5.06 |
| 41 |  |  | 81.4 | 122-123 | 4.41 4.45 | $C_{20}H_{13}N_2O_4IBr_2$ | 4.43 |

The reaction was carried out under nitrogen, in a system of organic solvents $CH_3OH +$ ether + Dimethylformamide. When choosing a solvent for this reaction, the following criteria were taken into account: stability in the temperature range used, the ability to dissolve the initial materials and reaction products well, the absence of chemical interaction of the solvent with the initial materials and reaction products, the absence of a negative effect on the catalyst activity, the purity of the solvent, and the effect of solvent on the substitution mechanism.

Protic solvents, in contrast to dipolar aprotic (Dimethylformamide), reduce the nucleophilicity of anions, at the same time contributing to the ionization of polarized bonds. It is assumed that the slowest stage of this reaction is the removal of the proton by the base, and therefore this reaction should proceed faster in dipolar aprotic solvents.

Thus, the specified choice of solvents makes it possible to create conditions for maximum yield of the reaction products. Besides, the haloid component in the reaction must be introduced gradually, since in the case of adding in large portions, its concentration in the reaction medium increases, resulting in occurrence of a side reaction and a decrease in the yield of the target product.

As catalysts we used various cuprous copper halide: Cu_2Cl_2 , Cu_2Br_2 , Cu_cI_2 . The most resultative was copper chloride. It is explained by the fact that the catalytic activity increases with the increase in the polarity of the bond in copper salts: $Cu_cI_2 > Cu_2Br_2 > Cu_2Cl_2$.

At the same time, we studied the effect of the catalyst amount on the reaction. The use of the catalyst in the amount of 1-2% to the initial compound provided a low concentration of copper ions (Cu^+) in the reaction medium. The copper ion, being freed from condensation, returned to the cycle, again forming a copper complex with free propargyl ether. The use of the catalyst in excessive amounts did not result in the desired outcome, since was accompanied by the side reaction.

As γ -bromopropargyl ether of carbamate derivatives is involved in the reaction, hydrogen bromide was released during the reaction. To neutralize the evolved hydrogen bromide, the reaction was carried out in the presence of a base. Primary, secondary, and tertiary amines of various structures were used as the base. The results showed that the primary amine was the best base. When using propyl- and butylamines, diacetylene ethers were formed with a yield of 90.1%, and when using diethylamine - up to 19%, and triethylamine - only 12%. The effect of amines on the dimerization reaction decreased in the following order: primary > secondary > tertiary. The reason for this effect of amines on the dimerization reaction was apparently related to their structure: when secondary and tertiary amines were used, insoluble acetylenide was formed and, due to this, the yield of diacetylene ethers was very low.

During the experiment, we also studied the effect of temperature on dimerization. It was established that the optimal temperature was 20°C. When the reaction was carried out at a low temperature, the product was obtained in low yield. This is apparently due to a decrease in the reagents reactivity. The temperature increase (35°C) is also accompanied by the decrease in the yield due to partial resinification of the reaction products.

The structure of the obtained diacetylene ethers was proved by the data of infrared spectroscopy and elemental analysis.

The infrared spectra of all the obtained compounds are characterized by the presence of the following absorption bands in the range of 1700-1740 cm^{-1} for the carbamate group, in the range of 2130-2200 cm^{-1} for the conjugated acetylene bond, and in the range of 3290-3340 cm^{-1} for the NH group.

It should be noted that the spectrum of all the obtained diacetylene ethers of carbamate derivatives had no absorption bands characteristic of valence vibrations of the terminal methine bond, which confirms the formation of the proposed products.

Experimental chemistry

Synthesis of γ -bromopropargyl ether of *p*-chlorophenyl carbamate (II). To 1.75 g of propargyl ether of *p*-chlorophenyl carbamate, dissolved in 50 ml of methyl alcohol we added 2.23 g of CuBr_2 stirring at room temperature and left it for 24 hours.

After the specified time, the content of the flask was transferred into a beaker with a saturated solution of ammonium chloride and lixiviated with ether. After evaporation, the resulting product was a crystalline substance with melting point 81-82°C. Total yield made 79% of the theory.

Synthesis of 1,6-bis-(4-chlorophenyl carbamate) - hexadine-2,4 (X). 0.05 g of copper chloride was placed in a Scheidt globe with a stirrer, drop funnel and gas inlet tube and dissolved in 8 ml of *n*-propylamine. Treating with nitrogen, stirring intensively, we poured in a solution of 0.66 g of propargyl ether of 4-chlorophenyl carbamate. Then, the solution of 1.06 g of γ -bromopropargyl ether of 4-chlorophenyl carbamate was added dropwise via the dropping funnel for 30 minutes, periodically adding hydroxylamine hydrochloride.

At the end of the reaction, the product was taken to the beaker with acidified water and repeatedly lixiviated with ether. The ether extracts were combined and ether was distilled off. The crystalline substance in the residue was purified by chromatography. Melting point made 105-106°C. The yield reached 74.5%.

Synthesis of [1- (4-chlorophenyl) -6- (2,4-dichlorophenyl) -carbamate] -hexadine-2,4 (XXIV). 0.05 g of copper chloride was placed in the Scheidt globe with a stirrer, drop funnel and gas inlet tube and dissolved in 8 ml of normal-propylamine. Treating with nitrogen, stirring intensively, we poured the solution of 0.66 g of propargyl ether of 4-chlorophenyl carbamate. Then, the solution of 1.06 g of γ -bromopropargyl ether of 2,4-dichlorophenyl carbamate was added dropwise via a drop funnel for 30 minutes, periodically adding hydroxylamine hydrochloride.

At the end of the reaction, the product was taken to the beaker with acidified water and repeatedly lixiviated with ether. The ether extracts were combined and ether was distilled off. The crystalline substance in the residue was purified by chromatography. Melting point was 85-86°C. The yield made 73.4%.

The obtained diacetylene ethers of carbamate derivatives were studied for various biological activity. As it is known from the literature data, the presence of carbamate group and a triple bond in a substance molecule promotes the manifestation of biological activity.

Antifungal activity of the synthesized compounds

The synthesized γ -bromopropargyl ethers were tested for antifungal activity. Preliminary studies were carried out by the diffusion method on a two-layer agar gel of weighed samples 1, 5, 10 mg.

The fungicidal action was studied on the following types of fungi: *Penicillium waksmani*, *Trichoderma Ronihgc*, *Alternaria Fenius*, *Aspergillus flayus*, *Fusarium moniliforme*.

Among the tested compounds, the most effective was the γ -bromopropargyl ether of 4-iodophenyl carbamate (VIII). The weighed sample 1 mg, when tested in the agar gel, inhibited the growth of the above fungi in the area of 20-38 mm.

By the method of dilutions in broth (Czapek liquid medium), the fungistatic effect of γ -bromopropargyl ether of 4-iodophenyl carbamate in dilutions of 1:4000-8000-16000-64000 was established, in which the content of the sample was 1250-626-362.5-90.625 μg per mg of nutrient medium respectively for *Penicillium waksmani*, *Trichoderma Ronihgc*, *Aspergillus flayus*, *Fusarium moniliforme*.

Thus, it has been established that γ -bromopropargyl ether of 4-iodophenyl carbamate had antifungal effect.

Herbicidal activity

Along with antifungal activity, the synthesized compounds were tested for herbicidal activity.

The primary herbicidal properties of γ -bromopropargyl ethers were established by sowing various plants in square containers measuring 30x40x20 cm, with a capacity of 20 kg of soil (gray soil). Soil moisture was maintained constant (65% of full moisture capacity) by daily irrigation. The objects of research were: as cultivated plants – cotton and corn; weed plants - panic grass, green amaranth. On the day of sowing the seeds, the soil surface in the containers was treated with the preparation at the rate of 6-10 kg / ha. Under the same conditions, seeds were sown in the control containers without preparation treatment. Calculation was carried out after 100% emergence of seedlings in control containers. The experiment was repeated four times. The effectiveness of the preparation was determined by calculating the number of affected plants, as well as by changing the weight of the underground mass of weed plants.

Thus, it was established that the studied compound γ -bromopropargyl ether of 2,4-dibromophenyl carbamate (VI) has a selective herbicidal activity, destroying the green amaranth for 84.5%, increasing the growth rate of cultivated plants, particularly cotton.

4. CONCLUSIONS

1. Convenient methods have been developed for obtaining new γ -bromopropargyl ethers of carbamate derivatives
2. New simple diacetylene ethers of carbamate derivatives were synthesized by the reaction of interaction on the basis of propargyl ethers and γ -bromopropargyl ethers of carbamate derivatives.
3. New asymmetric diacetylene ethers of carbamate derivatives were synthesized by carrying out the reaction of interaction based on propargyl ethers and γ -bromopropargyl ethers of various carbamate derivatives.
4. Based on the study of various factors effect (temperature, nature of the solvent, nature of the base and the catalyst) on the yield of the target products, the optimal conditions for their synthesis have been established.
5. The biological activity of the new synthesized compounds was studied and analyzed. It was revealed that the synthesized new derivatives of carbamates have a wide spectrum of antifungal activity. In addition, it was determined that the compound γ -bromopropargyl ether of 4-iodophenylcarbamate has an antifungal effect. The compound γ -bromopropargyl ether of 2,4-dibromophenylcarbamate (VI) has selective herbicidal activity.

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